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(2×2) reconstructions of the {111} polar surfaces of GaAs

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Ab initio total-energy calculations were used to examine (2×2) reconstruction models for the (111) and $(\bar{1}\bar{1}\bar{1})$ surfaces of GaAs. For the (111) surface the lowest-energy Ga-vacancy geometry is determined; several mechanisms for Ga-vacancy formation are examined and other reconstructions are discussed. For the $(\bar{1}\bar{1}\bar{1})$ surface it is shown that the As-vacancy model is unlikely and other geometries are considered.

The surfaces of crystalline solids usually exhibit a symmetry different from that of bulk atomic planes of the same orientation. The surface atoms are displaced from their ideal positions and produce an equilibrium structure of lower energy. This reconstruction, which leads to rehybridization of the surface bonding orbitals, strongly affects the electronic properties of the material. One might expect such reconstructions to be particularly important for polar surfaces, where they could decrease the surface polarity. Within the past year there has been considerable activity focused on determining the exact equilibrium geometry of the {111} surfaces of III-V semiconductors.[1-5] In particular, several structural models have been proposed[1,2,6-8] to account for the diffraction patterns observed on GaAs, of which the most popular seems to be the vacancy buckling geometry.[1,2] However, a realistic theoretical evaluation of the proposed models is lacking, because first-principles, self-consistent calculations were not feasible up to now because of the large unit cells required and the complications to self-consistency arising from the polarity of the surface.

In this paper we present a self-consistent, energy-minimization calculation in which the only input is the valence charge of the atoms. We thus determine the lowest-energy vacancy geometry and find that, contrary to the predictions of semiempirical calculations,[2] vacancy formation by removal of Ga atoms from the (111) surface is *endothermic*. Alternative mechanisms by which vacancy formation may proceed exothermically are investigated, and various model geometries are examined. Finally, we show that As-vacancy formation on the $(\bar{1}\bar{1}\bar{1})$ surface is unlikely and find other energetically favorable alternatives.

In order to study the different reconstruction geometries, we calculate the total energy of each configuration, using the self-consistent local-density functional formalism,[9] with the Wigner approximation[10] for the exchange-correlation energy and norm-conserving atomic pseudopotentials.[11] The calculation in the momentum-space representation[12] involves a basis of plane waves with energy up to 4 Ry (~1700 plane waves). An additional set of plane waves with energy up to 8 Ry (~3500 plane waves) is included by second-order perturbation theory.[13] These energy cutoffs are sufficient for accurate surface calculations as established elsewhere.[14] The surface is modeled by a slab geometry of 16 atomic layers plus a vacuum region equivalent to four bond lengths. Inversion symmetry is imposed to ensure that there are no artificial fields in the vacuum. As a consequence of the inversion symmetry the two central atomic layers of the slab contain the same kind of atoms. These layers are modeled by fractionally charged atoms which are properly chosen to prevent charge transfer from the central region to the surface or vice versa. The central layers, plus an additional six atomic layers representing bulk GaAs, are frozen throughout the calculation. Tests using different system sizes revealed that this approach works extremely well for the comparison of energies of various surface structures.

Figure 1 presents a perspective view of the (111) surface of GaAs. The ideal, unreconstructed surface consists of a plane of Ga atoms in a triangular lattice. A (2×2) periodicity can be created when one out of four surface atoms breaks the ideal symmetry. The parallelograms in Fig. 1 indicate the (2×2) unit cell, with the symmetry-breaking atom drawn cross hatched.

We consider first the vacancy buckling model.[1,2] The reconstruction affects the first four atomic layers and the imposed threefold rotational symmetry about the center of the (2×2) unit cell restricts the number of relaxation parameters to 11, labeled l_i, $i=1,\ldots,4$ (lateral) and v_i, $i=1,\ldots,7$ (vertical) in Fig. 1. The lowest-energy geometry is obtained by judiciously varying the relaxation parameters independently. The resulting parameter values are tabulated in Table I, along with the values describing the geometries proposed by Tong, Xu, and Mei[1] and by Chadi.[2]

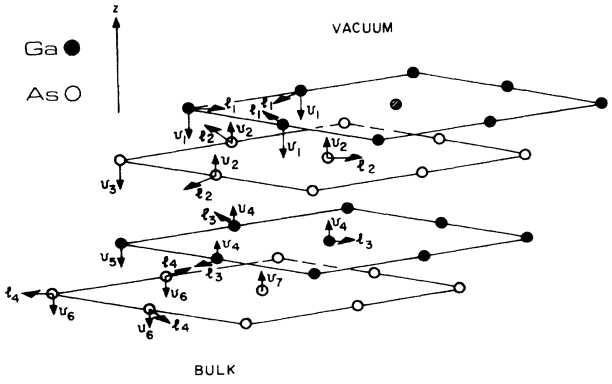

FIG. 1. Perspective view of the (111) surface with the vacancy relaxation parameters l_i, $i=1,\ldots,4$ and v_i, $i=1,\ldots,7$.

TABLE I. Relaxation parameters (in Å, as defined in Fig. 1) for three Ga-vacancy model geometries.

	Tong *et al.* (Ref. 1)	Chadi (Ref. 2)	This work
l_1	0.100	0.148	0.121
l_2	0.280	0.295	0.288
l_3	0.0	0.023	0.008
l_4	0.0	0.009	0.007
v_1	0.706	0.582	0.630
v_2	0.040	0.059	0.064
v_3	0.080	0.078	0.029
v_4	0.010	0.060	0.063
v_5	0.080	0.052	0.039
v_6	0.0	0.004	0.003
v_7	0.0	0.052	0.021

We define the relaxation energy as the energy lowering with respect to the unrelaxed vacancy geometry. Our calculations for the three different geometries indicate that the configuration obtained by this work reduced the energy by ~ 0.15 eV. This lowest-energy geometry also has minimal bond strain, defined as the deviation of the bond length from the bulk value (Table II).

The driving mechanism for relaxation of the vacancy model is the rehybridization of the bonding orbitals in the first bilayer. The removal of one surface Ga atom per (2×2) unit cell leaves equal numbers of Ga and As dangling bonds (three of each kind) and the relaxation eliminates all of them by transforming the As dangling bonds into *s*-like fully occupied states and the Ga dangling bonds into p_z-like empty states. In the final geometry the surface Ga atoms are in a sp^2-bonding configuration, almost planar with the first bilayer As atoms, while three of these As atoms are in a p^3-bonding configuration (cf. Table II).

In order to study the energetics of vacancy formation we first consider the possibility of gradually displacing one Ga atom per (2×2) unit cell out of the surface or into the bulk. The remaining atoms are then allowed to relax accordingly. The energy of the different configurations versus the position of the Ga atom on the *z* axis is plotted in Fig. 2 (solid dots). As the Ga atom is displaced toward the vacuum, the energy initially decreases. However, it soon begins to rise rapidly, resulting in an *endothermic* removal energy of 2.5 eV. This is in contrast to the only other available theoretical estimate[2] of an *exothermic* removal energy of −0.2 eV. Furthermore, movement of the Ga atom toward the bulk is inhibited by a large energy barrier. The local energy maxima at $z = -0.8$ and -4.0 Å correspond to geometries where the Ga atom crosses the planes of As atoms in the first and second bilayers.

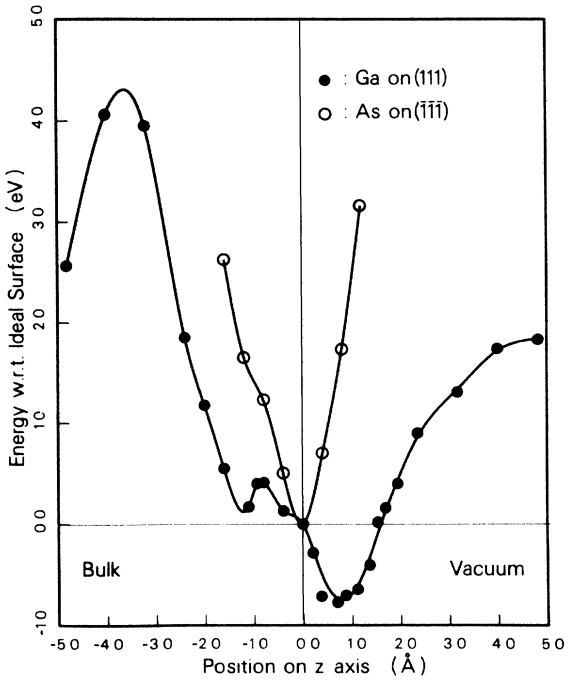

FIG. 2. Relaxed surface total energy per (2×2) unit cell as a function of the position on the *z* axis of the symmetry-breaking atom.

TABLE II. Relaxation energies, geometric properties, and the range of bond strains for three Ga-vacancy model geometries.

	Tong *et al.* (Ref. 1)	Chadi (Ref. 2)	This work
Relaxation energy per (2×2) unit cell	3.16 eV	2.99 eV	3.31 eV
Average angle of sp^2-bonded Ga	119.8°	119.2°	119.7°
Average angle of p^3-bonded As	92.9°	93.8°	93.2°
Bond strain	+1.9%	+2.2%	+0.9%
	−1.3%	−1.1%	−1.0%

In Fig. 2 the minimum of the energy curve occurs at $z = 0.70$ Å, lower in energy than the ideal geometry by 0.8 eV. This corresponds to the buckled geometry[6] with the displaced Ga atom 1.05 Å above the plane of the three relaxed surface Ga atoms. The bonds of the buckled atom are stretched by 8%. Due to rehybridization, an *s*-like state associated with the buckled Ga atom is filled and the stretched bonds are weakened. The necessary amount of electronic charge to fill these bonds is provided by partial charge transfer from the remaining surface dangling bonds. The relaxation brings the surface Ga atoms close to the plane of As atoms and this, combined with the partial charge transfer, reduces the polarity of the surface.

We would now like to consider other surface reconstruction geometries which may have concentrations of Ga and As atoms different from the ideal surface and therefore we must include the relevant atomic reservoirs. We have studied in detail the As-substitutional[7] and the As-adatom[8] geometries. The substitutional geometry consists of an As atom replacing one surface Ga atom per (2×2) ideal surface cell, creating three As—As bonds. The adatom geometry consists of placing one extra As atom per (2×2) ideal surface cell above the center of the triangle formed by three surface Ga atoms. As sources and sinks for the Ga and As atoms, we have considered Ga gas, As_2 gas, Ga-metal droplets, and bulk GaAs. These reservoirs provide

appropriate choices for various experimental surface preparation conditions.[15] The reservoir energies to be used in our calculations were taken from experiment:[16] −2.8 eV per atom for the cohesive energy of bulk Ga, −2.0 eV per atom for the binding energy of As_2 molecules, and −6.7 eV per pair for the cohesive energy of bulk GaAs.

In Fig. 3 we illustrate the energies of the different geometries, along with the corresponding reservoirs, relative to the *ideal surface*. For the vacancy model, removing the Ga atom to a Ga gas reservoir is energetically unfavorable by 1.7 eV. As described earlier, this corresponds to an endothermic removal energy of 2.5 eV with respect to the *buckled geometry*. However, if the Ga atom is placed in a Ga-metal droplet, vacancy formation becomes exothermic. Finally, if excess As_2 gas is available, formation of GaAs bulk pairs can lead to an even lower-energy configuration. We note that the As-substitutional and As-adatom geometries do not compare favorably with the vacancy geometry. In fact, the most interesting feature of Fig. 3 is that irrespective of experimental conditions (which lead to the presence of excess As or Ga atoms) the vacancy geometry has the lowest energy of all the models proposed so far. A combination of the vacancy and adatom geometries is not favored because the respective relaxations oppose each other.

We turn now to a discussion of the $(\bar{1}\bar{1}\bar{1})$, As-terminated surface. A (2×2) reconstruction pattern has been observed on this surface as well,[3,15] and in Fig. 4 we summarize the (2×2) geometries studied along with the appropriate atomic reservoirs.

A detailed search over the relaxation parameter space was performed to determine the optimal As-vacancy geometry which consists of displacements opposite from those on the (111) surface. The highest relaxation energy obtained was

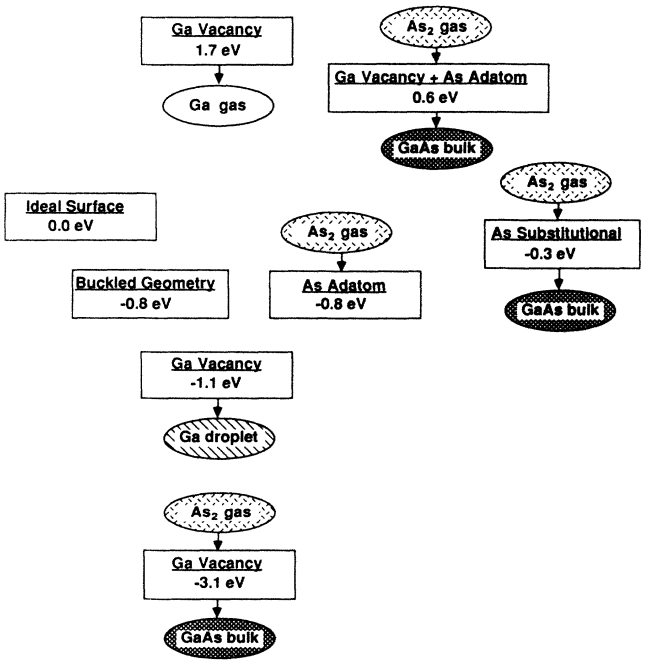

FIG. 3. Total energy per (2×2) unit cell of various reconstruction models for the (111) surface of GaAs.

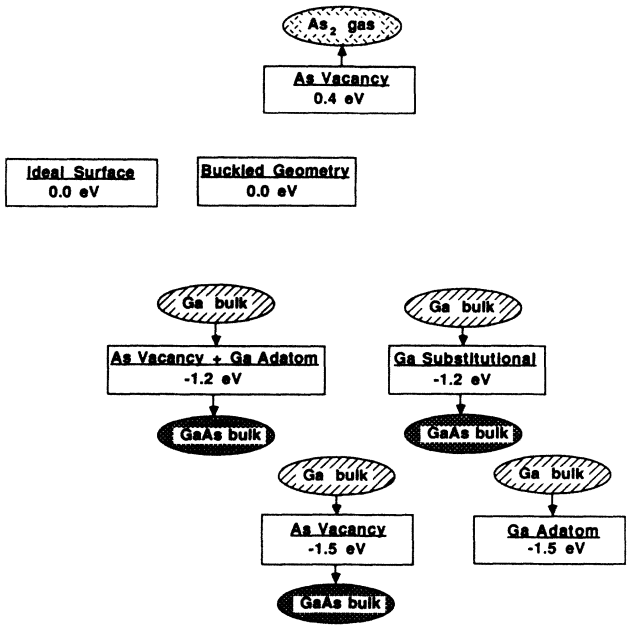

FIG. 4. Total energy per (2×2) unit cell of various reconstruction models for the $(\bar{1}\bar{1}\bar{1})$ surface of GaAs.

2.04 eV per (2×2) unit cell which is considerably less than the corresponding value for the Ga vacancy (3.31 eV). This is a purely geometric effect since the optimal relaxation of the As vacancy cannot produce the almost perfect coordination for the surface atoms achieved in the Ga-vacancy model. For the vacancy model, removing the As atom to an As_2 gas reservoir is endothermic by 0.4 eV, whereas the presence of excess Ga gas allows for the possibility of GaAs bulk pair formation which leads to an overall exothermic process. However, the energetics associated with the displacement of an As atom outward or inward from the surface make the As-vacancy model unlikely: The energy increases steeply and monotonically for displacement in either direction as seen from Fig. 2 (open circles).

An interesting reconstruction for the $(\bar{1}\bar{1}\bar{1})$ surface is the Ga-adatom geometry.[7] We find that in the optimal geometry the extra Ga atom is situated 1.2 Å above the center of the triangle formed by three surface As atoms and forms bonds stretched by 6.7% of the bulk value. This configuration is 1.5 eV lower in energy than the ideal surface. The absence of any energy barrier for this geometry makes it a likely alternative to the As-vacancy geometry which gives equal energy gain (see Fig. 4).

Two other geometries for the $(\bar{1}\bar{1}\bar{1})$ surface, which are within our estimated calculational uncertainty (0.3 eV) from the lowest-energy reconstructions, are the Ga-substitutional geometry and a combination of the As vacancy and Ga adatom (Fig. 4). The substitutional geometry consists of a Ga atom replacing a surface As atom and forming three coplanar Ga—Ga bonds. The vacancy and adatom geometries for the $(\bar{1}\bar{1}\bar{1})$ surface have relaxations which are mutually compatible allowing for the formation of a low-energy combination. We note, however, that both of these geometries may require the formation of an As vacancy as an intermediate step. The possible high-energy barrier of this process suggests that kinetics may have substantial influence in

determining the equilibrium surface structure. In particular, if kinetics is important, only the Ga adatom would be favorable and in a saturated environment Ga adatoms should completely cover the surface. If kinetics is not crucial, other geometries requiring removal of As atoms from the surface (e.g., As vacancy, Ga substitutional, etc.) are attainable, and the presence of excess Ga should produce a Ga-rich surface, due to As vacancies, Ga substitutionals, Ga adatoms, and possible combinations of these configurations. Finally, our search for a surface model stabilized by excess As_2 gas has not yielded an interesting alternative thus far.

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